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Doping dependent metal to insulator transition in the (Bi, Pb)-2212 system: The evolution of structural and electronic properties with europium substitution*

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The present work investigates the effect of europium substitution on the (Bi, Pb)-2212 system in the concentration range $0.5 \leq x \leq 1.0$. Phase analysis and lattice parameter calculations on the powder diffraction data and the elemental analysis of EDX show that the Eu atoms are successfully substituted into the (Bi, Pb)-2212 system. Resistivity measurements (64–300 K) reveal that the system exhibits superconductivity at $x \leq 0.5$ and semiconductivity at $x > 0.5$. With the complete suppression of superconductivity which is known to be a quasi-two dimensional phenomenon in these materials, a metal to insulator transition takes place at $x = 0.6$ and the predominant conduction mechanism is found to be variable range hopping between localized states, resulting in macroscopic semiconducting behaviour. The results of electrical and structural properties of the doped (Bi, Pb)-2212 compounds suggest that the decrease of charge carrier concentration and the induced structural disorder are the more effective and dominant mechanisms in the origin of the metal to insulator transition and suppression of superconductivity due to Eu substitution at its Sr site.

Keywords: (Bi, Pb)-2212 superconductor, metal to insulator transition, variable range hopping, electrical properties

PACC: 7470V, 7465, 7130, 7430E

1. Introduction

The high T_c cuprate superconductors (HTSCs) constitute a special group of materials that share many common features in crystal structures and properties. One of the characteristic features is that they have layered crystal structures with the Cu–O_2 layer as the most essential structural unit. It is well established that the charge carriers (holes for p type) are mainly confined to the two dimensional (2D) Cu–O_2 layers.[1] These HTSCs are one of the most intensively studied systems due to their anomalous, normal and superconducting properties which are closely related to metal to insulator transitions (MITs). The parent cuprates are anti-ferromagnetic insulators and superconductivity appears with carrier doping. Some of the recent work shows that different cationic substitutions at different sites in a cuprate system can lead to a change in charge carrier concentration and increase in disorder in the system.[2−5] In the presence of sufficient disorder the dynamics of electron–electron interaction becomes important,[6] affecting the final pairing and ultimately resulting in a MIT.[7,8] The strong electron correlation and disorder can cause carrier localization and produce MITs in doped systems which are respectively known as Mott and Anderson transitions.[9,10] So, exploring the effects of dopants in high temperature superconductors (HTSCs) is an important tool in understanding their superconducting and normal state properties.

Since the discovery of the HTSC, Bi–Sr–Ca–Cu–O, an exhaustive study of this class of materials has been carried out and in the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ system, three superconducting phases with $n = 1$, 2, or 3 have been isolated. The index 'n' is related to the number of Cu–O_2 layers in the unit cell. Furthermore, the critical temperature increases with an increasing number of these consecutively stacked layers. However, even for the same index n, the superconducting properties depend on the hole concentration. So the effect of change in charge carrier concentration is one of the crucial parameters in the

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study of superconducting cuprates because it predominantly determines various physical properties of the system, such as the transition temperature, electrical and magnetic properties etc. Most of the investigations on Bi–Sr–Ca–Cu–O high T_c superconductors are focused on the composition range where the samples are superconducting,[11,12] and no effort has been undertaken so far to study the non-superconducting concentrations. To understand superconductivity, it is important to know the origin of insulating states as well as the basic character of the metallic state induced by cation substitution.

In order to achieve a better understanding of the role of the rare-earth (RE) atom in high temperature superconductivity, and to reveal their mechanisms, we have prepared oxides with compositions $Bi_{1.7}Pb_{0.4}Sr_{2-x}Eu_xCa_{1.1}Cu_{2.1}O_{8+\delta}$ ($0.5 \leq x \leq 1.0$) and performed a detailed characterization of their physical and electronic properties as a function of x. Here we focus our attention on the superconducting and nonsuperconducting composition range of the Bi-2212 samples by doping it with both lead and a rare-earth, europium (Eu). It is experimentally shown that Pb substitution at the Bi-site in Bi-2212 significantly reduces the electromagnetic anisotropy and improves the c-axis conductivity, thereby improving the coupling between the Cu–O_2 layers without any change in T_c.[11,12] Thus it is expected that the combined effect of Pb co-doping at the Bi-site associated with RE substitution in Bi-2212 could enhance the superconducting properties such as T_c as well as J_c of the system. In this paper special attention is paid to the MIT phenomenon on the basis of the effect of charge carrier concentration and disorder because MITs in the hole doped Bi–Sr–Ca–Cu–O would be an important clue to elucidate the mechanism underlying high T_c superconductivity.

2. Experimental

Eu substituted (Bi, Pb)-2212 samples were prepared by the conventional solid state synthesis method with an initial stoichiometry of $Bi_{1.7}Pb_{0.4}Sr_{2-x}Eu_xCa_{1.1}Cu_{2.1}O_{8+\delta}$ ($x = 0.5$, 0.6, 0.7, 0.8, 0.9 and 1.0). Stoichiometric quantities of high purity (Aldrich > 99.9%) chemicals such as Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, Eu_2O_3 and CuO were accurately weighed using an electronic balance (Mettler AE 240). The ingredients were further homogeneously ground, using a planetary ball mill (FRITSCH Pulversette 6). The samples were calcined in air atmosphere at 800 °C/20 h+820 °C/40 h+840 °C/60 h and intermediate grinding in acetone medium was done between stages of calcination to improve the homogeneity of the samples. The samples were then pelletized using a cylindrical die of 12 mm diameter, under a force of 80 kN and electrical contacts were made on the surface of the pellets by placing thin silver strips at this stage. The pellet samples were heat treated at 885 °C for 120 h (60 h+60 h), with one intermediate re-pressing under the same stress.

Phase analysis of the samples was done using XRD (Philips X'pert Pro) equipped with a monochromator at the diffracted beam side. Microstructural examination and elemental analysis of the samples were done using SEM (JEOL JSM 5600 LV) equipped with EDX. The critical temperature of the samples was determined by the four probe dc electrical resistance method. We label the $Bi_{1.7}Pb_{0.4}Sr_{2-x}Eu_xCa_{1.1}Cu_{2.1}O_{8+\delta}$ samples with $x =$ 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 as Eu5, Eu6, Eu7, Eu8, Eu9, Eu10, respectively.

3. Results and discussion

The powder x-ray diffraction patterns of samples after the last stage sintering process are displayed in Fig.1. All the samples show a single phase behaviour consisting of (Bi, Pb)-2212 and no peaks of any secondary phases are observed, even up to $x = 1.0$. This indicates a complete solubility of Eu in the $Bi_{1.7}Pb_{0.4}Sr_{2-x}Eu_xCa_{1.1}Cu_{2.1}O_{8+\delta}$ system and its successful substitution in the crystal structure of

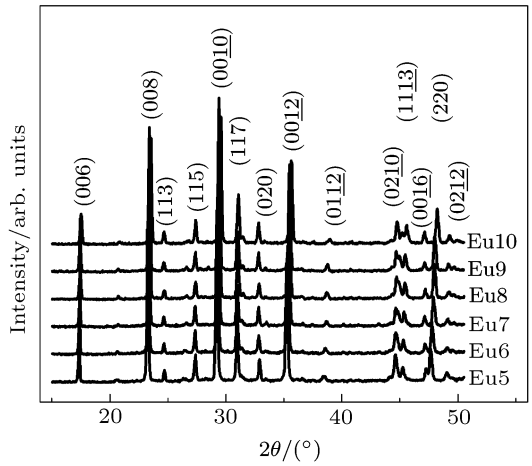


Fig.1. XRD patterns of the samples after heat treatment at 885 °C for 120 h.

the (Bi, Pb)-2212 system. The major peaks of (Bi, Pb)-2212 have been indexed in the pattern, by as-

suming an orthorhombic symmetry for the unit cell.

Energy dispersive x-ray (EDX) analysis was further used to identify the different elements present in the samples and to confirm the substitution of Eu in the (Bi, Pb)-2212 system. Figure 2 shows the EDX patterns of a pure (Bi, Pb)-2212 grain and a typical Eu substituted (Bi, Pb)-2212 grain [Eu10]. The presence of Eu is detected in the Eu substituted (Bi, Pb)-2212 grains with a corresponding reduction in the Sr content. This confirms that Eu atoms are successfully substituting at the Sr sites of (Bi, Pb)-2212.

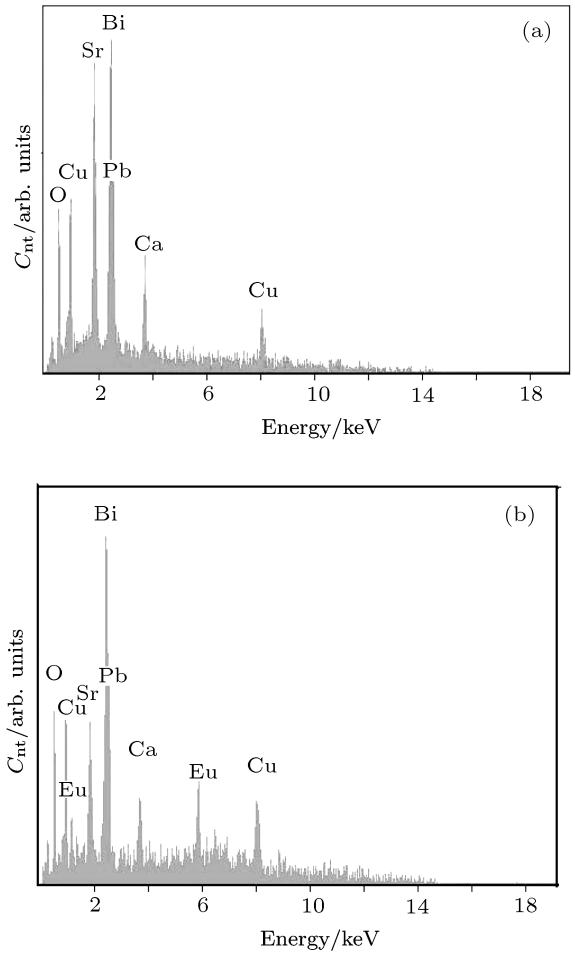


Fig.2. EDS of pure (a) and Eu substituted (b) (Bi, Pb)-2212 grain.

The calculated lattice parameter values of the samples are shown in Fig.3. There is a systematic increase in the a and b lattice parameters with increasing Eu content, x. Moreover the difference between the a and b lattice parameters is small. The elongation of a/b is as expected because the extra electrons introduced by the doped Eu atoms increase the effective valence of Cu. This in turn increases the Cu–O bond length which manifests as the increase in the a/b lattice parameter. The c lattice parameter decreases with x and this may be understood on the following basis. As the Eu^{3+} content increases, the interlayer distances Cu–Ca–Cu and Ca–Sr expand but Sr–Bi, Bi–Bi and Sr–Bi–Bi–Sr shrink because the extra oxygen resides in the Bi–O double layers. This extra oxygen balances the increased valency due to the replacement of Sr^{2+} by Eu^{3+}. Consequently, the net positive charge in the Bi–O layers reduces. Hence, the repulsion between them is reduced and the distance between the layers in the structure contracts. Also, the replacement of the larger Sr ion (1.18 Å) by a smaller Eu (0.947 Å) ion should result in contraction of the c axis.

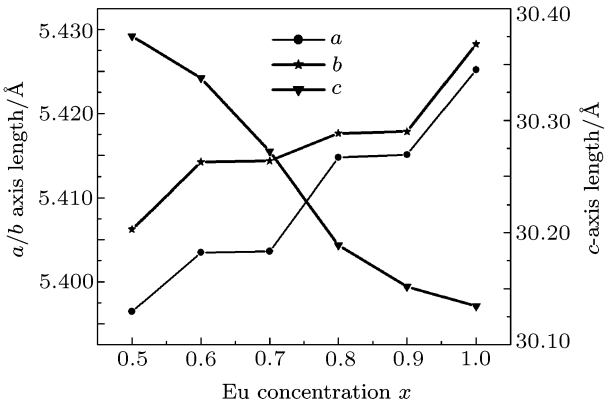


Fig.3. Variation of lattice parameters with Eu concentration.

Figure 4 shows SEM micrographs of the fractured surface of the Eu doped samples. All the samples have similar microstructure with a characteristic flaky grain structure, typical of (Bi, Pb)-2212. But with the increase in x, the grain size decreases. This shows that Eu substitution does not deteriorate the microstructure of (Bi, Pb)-2212 system.

The temperature dependence of the electrical resistivity of the $Bi_{1.7}Pb_{0.4}Sr_{2-x}Eu_xCa_{1.1}Cu_{2.1}O_{8+\delta}$ samples, normalized to their room temperature value, $(\rho(T)/(\rho(300))$ is shown in Fig.5. The resistivity behaviour of these samples may be divided into three parts.

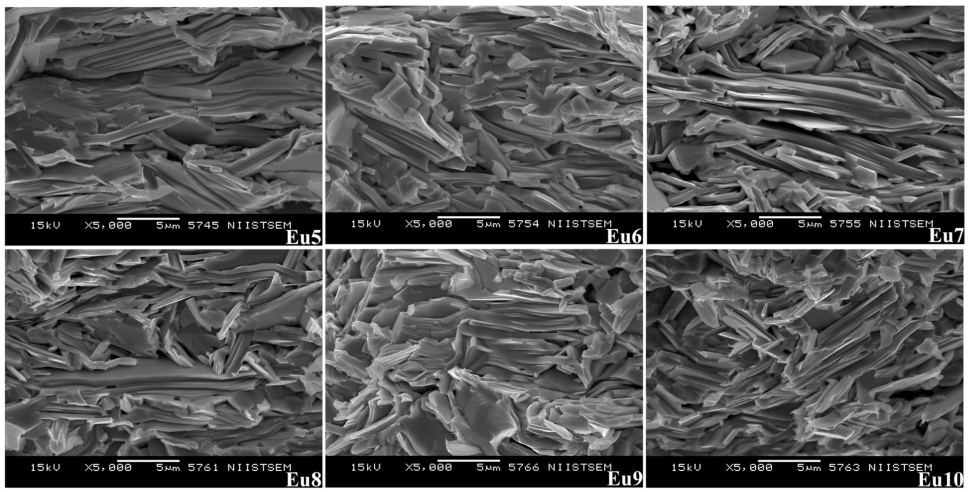


Fig.4. SEM micrographs of Eu substituted (Bi, Pb)-2212 samples.

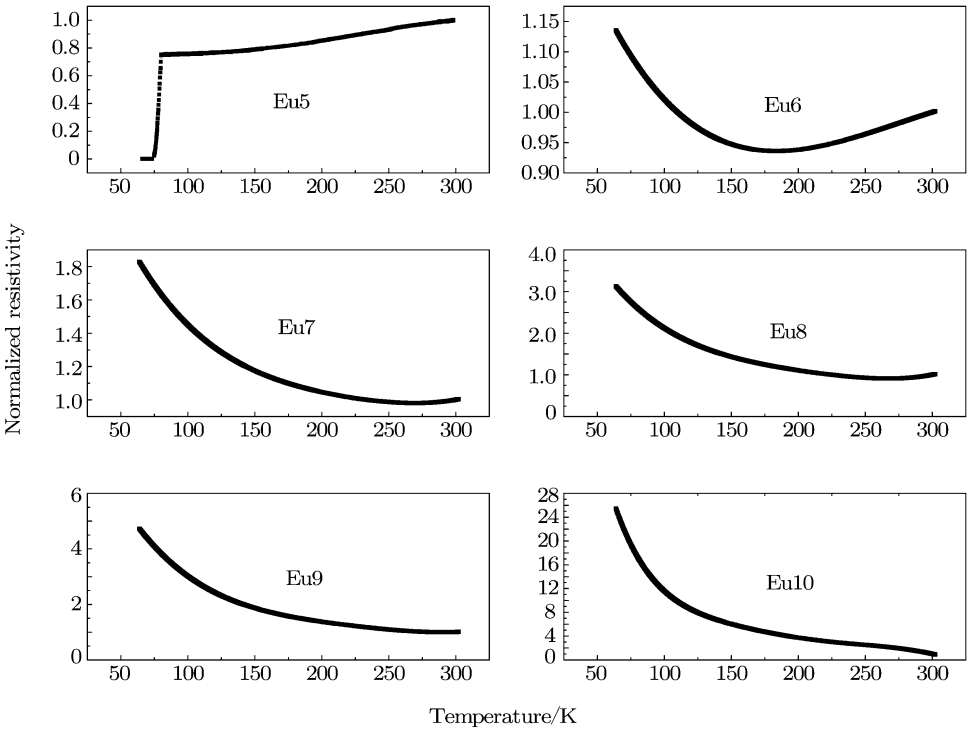


Fig.5. Variation of normalized resistivity of the samples with temperature.

a) The sample with $x = 0.5$ shows metallic behaviour in the normal state, followed by a superconducting transition temperature. The observed T_c = 80.16 K. In the temperature range 82 K$\leq T \leq$ 300 K, the resistivity data fits well with the expression $\rho(T) = \rho(0) + bT$, where $\rho(T)$ is the resistivity of the sample at a particular temperature T and $\rho(0)$ is the residual resistivity.

b) For the samples Eu6, Eu7, Eu8 and Eu9, a minimum in the resistivity ($\rho_{\min}$) is observed at temperatures ($T_{\min}$) around 184.05 K, 270.39 K, 272.64 K and 290.37 K respectively. Above this temperature $T_{\min}$, these samples show metallic properties and below this, they exhibit semiconducting behaviour.

c) The sample Eu10 is semiconducting in the entire temperature range. In this sample $\rho_{\min}$ occurs at a higher temperature which is likely above room temperature.

All these observations indicate that there is no superconducting transition for samples with $x > 0.5$ in the measured temperature range (64 to 300 K) and a MIT takes place at $x = 0.6$ with suppression in the superconductivity. The normal state resistivity of the samples at any particular temperature, $T > T_c$ increases with the Eu concentration x. It is necessary to determine the behaviour of the charge transport in these semiconducting samples because it provides diverse information such as electronic correlation and the density of states. The increase in resistivity of the insulating samples cannot be ascribed to the thermally activated conduction but it can be described by the variable range hopping (VRH) conduction between the localized states. The empty sites can be filled at low temperatures. In hopping conduction, the temperature dependence is generally weaker than $\exp(-1/T)$ which is thermally activated conduction. The hopping conduction is associated with the electron jumping from an occupied site to empty ones. The well known examples for hopping conduction are due to Mott,[13] and Shklovskii and Efros.[14] They have given the temperature dependence of resistivity as

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\alpha} \tag{1}$$

and

$$\alpha = \frac{(n+1)}{(n+d+1)} \tag{2}$$

where 'd' is the dimensionality of the hopping process and 'n' describes the energy dependence of the density of states near the Fermi energy $N(E_F)$, ρ_0 and T_0 depends on the shape of localization of the hopping site, the form of tunnelling probability and the energy dependence of the density of states. T_0 can be expressed as

$$T_0 = \frac{27}{(4\pi\xi^2 K_B N(E_F))} \quad \text{in two dimensions} \tag{3}$$

and

$$T_0 = \frac{16}{(\xi^3 K_B N(E_F))} \quad \text{in three dimensions.} \tag{4}$$

Here ξ is the localization length near the Fermi level.

It is very difficult to determine a unique value for α. However, for an energy independent density of states ($n = 0$), we can write $\alpha = 1/3$ in two dimensions and $\alpha = 1/4$ in three dimensions in the Mott VRH case, whereas in the Shklovskii and Efros case, $n = 1$ for 2D and $n = 2$ for 3D which leads to the

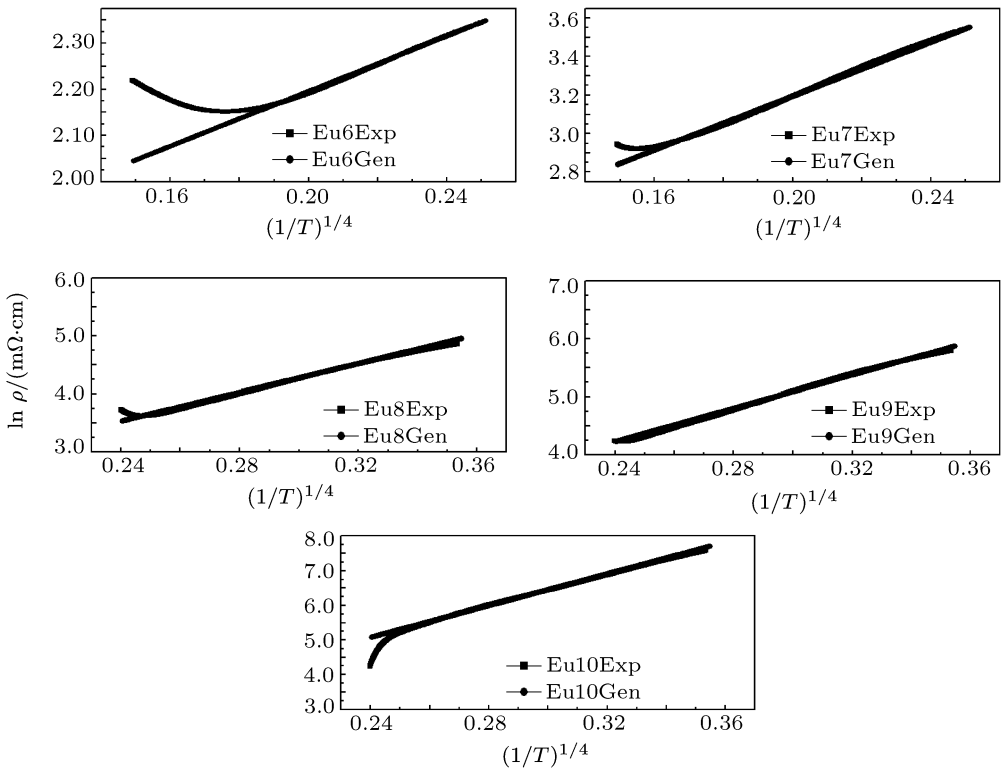


Fig.6. Best fit of the samples with ln ρ vs $(1/T)^n$ (Exp: denotes the experimental data and Gen: denotes generated data).

same exponent $\alpha = 1/2$. The least square fitting of $\ln \rho$ vs $(1/T)^{\alpha}$ for $\alpha = 1/2$, $1/3$ and $1/4$ in the present samples showed the best fit for $\alpha = 1/3$ in the case of Eu6 and Eu7 samples and for Eu8, Eu9 and Eu10 samples, $\alpha = 1/4$. Figure 6 shows the fitting of the experimental data of all the samples in relation to the Eq.(1); T_0 and T are in unit of K. This indicates that the electrical conduction in samples Eu6 and Eu7 takes place by the 2D VRH whereas it is 3D VRH in Eu8, Eu9 and Eu10. The hopping parameters are given in Table 1. The systematic increase in T_0 value with increasing x indicates that the material becomes more and more disordered with the increase in dopant levels and there is a decrease in either the localization length or in the density of states at the Fermi energy. The localization length of the insulating samples is determined using Eqs.(3) and (4) and is given in Table 1.

Table 1. Hopping parameters.

sample	$1/\alpha$	ξ/Å	T_0/K
Eu6	3	0.0028	26.43
Eu7	3	0.0008	342.64
Eu8	4	8.8986	23381.84
Eu9	4	7.3097	41986.94
Eu10	4	3.9109	275705.94

The principal mechanism of T_c suppression in samples of $0.5 < x \leq 1.0$ is the charging effect due to the extra electron introduced at the Sr site by the Eu atoms. This electron fills the Cu 3d holes and hence disrupts the Cu 3d–O 2p hybridization which is believed to be the primary source for the formation of Cooper pairs and thus leads to the observed suppression of superconductivity. This view is supported by theoretical discussions based on the Anderson impurity model,[15] indicating that the electronic states near the Fermi level are itinerant for a large overlap of the Cu 3d and O 2p wave functions, but become localized when this overlap is reduced. The upturn in resistivity of the semiconducting samples with decreasing in temperature is attributed to the random distribution of Eu at the Sr site which induces disorder in the system. Since normal state resistivity is a measure of disorder, the systematic increase of normal state resistivity with x is related to the localization.

The crossover between hopping transport ($\mathrm{d}\rho/\mathrm{d}T < 0$) at low temperatures and metallic transport ($\mathrm{d}\rho/\mathrm{d}T > 0$) at high temperatures in samples Eu6, Eu7, Eu8 and Eu9 can also be understood if disorder caused by the random distribution of Eu at the Sr sites is taken into account. This disorder leads to non-periodic fluctuations in the crystal potential and can therefore cause localization of the electronic states in the tails of the conduction band. Hopping conductivity is governed by the hopping probability between occupied and unoccupied sites. At high temperatures the hopping probability is dominated by the random spatial distribution of the atomic sites. Whether the system is an insulator or metal depends on the position of the Fermi level E_F relative to the mobility edge E_C. The minimum indicates that in their ground state the carriers are localized and become delocalized only at elevated temperatures. Mott VRH is found in strongly localized systems in the absence of Coulomb interactions between electrons. So in the present samples it can be concluded that the influence of Coulomb interaction is negligible and the optimal hopping energy exceeds the width of the Coulomb gap at high temperatures.[16]

4. Conclusions

The effect of Eu doping on the structural and electronic properties of the (Bi, Pb)-2212 system was studied. Powder x-ray diffraction data and elemental analysis indicate the successful substitution of Eu^{3+} ions at the Sr site of the (Bi, Pb)-2212 system. A lattice parameter calculation shows that the a and b axis lengths increase with Eu concentration while the c axis length decreases with Eu doping. This can be explained by the higher valence of Eu ions substituting at the Sr site of the (Bi, Pb)-2212 system and by the incorporation of extra oxygen in the Bi–O layers. The resistivity measurements show that the sample with $x = 0.5$ is superconducting while with increasing Eu content, the metallic behaviour of resistivity of the samples (at $x = 0.5$) changes to insulating behaviour ($x > 0.5$) with a metal to insulator transition at $0.5 < x \leq 0.6$. The metal to insulator transition and the dominant superconducting suppression effect in samples $0.6 \leq x \leq 1.0$ are attributed to the filling of the Cu–O holes by the excess charge introduced by the Eu atoms and to the disorder induced by the random distribution of Eu atoms at the Sr site of (Bi, Pb)-2212 system. The electrical conduction in the semiconducting samples is in agreement with Mott's VRH mechanism in two dimensions for samples with $x = 0.6$, 0.7 and three dimensions for samples with $x = 0.8$, 0.9 and 1.0.

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